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(21) International Application Number: PCT/US91/09284 (22) International Filing Date: 10 December 1991 (10.12.91) (30) Priority data: 651,900 6 February 1991 (06.02.91) US (71) Applicant: ICI AMERICAS INC. [US/US]; 1200 South 47th Street, Box 4023, Richmond, CA 94804-0023 (US). (72) Inventors: SCHER, Herbert, B. ; 1028 Wickham Drive, Moraga, CA 94556 (US). RODSON, Marius ; 533 Chabre Court, El Sobrante, CA 94803 (US). (74) Agents: ACKERMAN, Joel, G. et al.; ICI Americas Inc., 1200 South 47th Street, Box 4023, Richmond, CA 94804-0023 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent), SU. Published <i>With international search report.</i>
(54) Title: MICROENCAPSULATED HERBICIDAL COMPOSITION (57) Abstract Capsules capable of controlled release of 2-chloro-N-(ethoxymethyl)-6'-ethyl-o-acetotoluidide herbicide enclosed in a polyurea capsule produced by the process comprising encapsulating waterimmiscible material within discrete capsules of polyurea without addition of a second reactant, whereby hydrolysis of an isocyanate monomer to form an amine takes place which in turn reacts with another isocyanate monomer to form polyurea, which comprises the steps of: a) providing, at room temperature, a dispersion of (i) a water-immiscible phase comprising the herbicide and an organic polyisocyanate in (ii) an aqueous phase comprising a solution of water, a surfactant and a protective colloid; and b) heating and maintaining said dispersion in a temperature range from about 40 °C to about 90 °C, whereupon said herbicide is encapsulated within discrete polyurea capsular enclosures. The microencapsulated composition performs comparably to non-encapsulated compositions of the same herbicide applied at the same application rates, while maintaining substantially lower mammalian toxicity compared with the nonencapsulated formulations.		

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MICROENCAPSULATED HERBICIDAL COMPOSITIONField of the Invention

This invention relates to microencapsulated herbicidal compositions containing a haloacetanilide herbicide, and processes for preparation and for use of such compositions.

Background and Prior Art

The haloacetanilides, particularly the subclass generally known as α -chloroacetanilides, are a well-known class of herbicidal agents and have been used and proposed for use in a number of crop and non-crop applications. Some of the better known members of this class include α -chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-acetanilide (metolachlor), N-butoxymethyl- α -chloro-2',6'-diethylacetanilide (butachlor), α -chloro-2',6'-diethyl-N-methoxymethylacetanilide (alachlor), 2-chloro-N-(ethoxymethyl)-6'-ethyl-o-acetotoluidide (aceto-chlor) and α -chloro-N-isopropylacetanilide (propachlor). Many other compounds of this type are disclosed in numerous patents.

Various patents and publications describe the production and application of microencapsulated formulations of haloacetanilide herbicides. These include U.S. Patents 4,280,833; 4,417,916; 4,534,783; 4,563,212; and 4,640,709. Additionally, U.S. Patent 4,936,901 discloses herbicidal compositions which are dry flowable water-dispersible granular formulations comprising a mixture of microcapsules of a water-insoluble pesticide (including a haloacetanilide herbicide) encapsulated within a polymeric shell wall and at least one other pesticide which is nonencapsulated.

In the patents just mentioned, the microcapsule is formed in general with a shell wall of polyurea which is prepared in general from an aqueous phase material containing, for example, an emulsifier, and a water-immiscible phase consisting essentially of polymethylene polyphenylisocyanate and

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a water-immiscible herbicide, such as a haloacetanilide herbicide. To that is added, with agitation, a polyfunctional amine, which reacts with the polyphenylisocyanate to form a polyurea shell wall around the water-immiscible phase. This basic process is described in U.S. Patent 4,280,833. The remaining patents and patent application describe improvements in the process or microcapsules formed, such as specific emulsifiers which may be used in preparation of these microcapsules.

Microcapsule formulations are employed to achieve a slow or controlled release of the material encapsulated (in the present case, a water-immiscible haloacetanilide herbicide) into the surrounding or external medium. When properly done, the results are greater longevity of the encapsulated material and longer availability of it for its intended purpose. In the case of herbicides, microencapsulation provides a means for obtaining longer effective life of the herbicide in the surrounding medium, for instance in the soil, through a controlled release.

This benefit of increased longevity, however, can be offset by lack of sufficient activity of the material in the early period after application, and/or at relatively low application rates. Presumably this occurs because shortly after application, or at low rates, or both, there has been insufficient release of the active material (e.g. herbicide) to provide effective results, particularly in comparison with similar material applied in nonencapsulated form.

A typical comparison of the behavior of encapsulated as opposed to nonencapsulated forms of haloacetanilide herbicides is found in Example 17 of U.S. Patent 4,280,833 (the same information is in Example 30 of U.S. Patent 4,417,916). This example compares the performance of encapsulated and nonencapsulated (emulsifiable concentrate) forms of the haloacetanilide herbicide alachlor at varying concentrations and over a period of time. In the procedure of this

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example, alachlor is applied to weeds planted in aluminum pans at application rates ranging from 1.0 lb./acre down to 0.0078 lb./acre. As the example states, the results indicate that microencapsulated alachlor exhibited longer soil longevity than unencapsulated alachlor applied at the same rates. However, the same example also indicates that at the first rating period, two weeks after planting, the activity of encapsulated alachlor began to decrease at application rates below 0.5 lbs./acre on barnyardgrass and below 0.25 lbs./acre on crabgrass and green foxtail. Indeed, at an application rate of 0.0625 lbs./acre, the encapsulated alachlor was rated "0" on barnyardgrass and green foxtail, whereas the unencapsulated alachlor received ratings of 100 and 70, respectively.

Another process for production of microencapsulated forms of pesticides, including herbicides, is disclosed in U.S. Patent 4,285,720. This process involves the preparation of microcapsules by a technique generally known as in situ interfacial condensation polymerization. In general, in the process described in U.S. Patent 4,285,720, microencapsulated formulations containing pesticides are prepared by the steps of (a) providing, ~~at room temperature, a dispersion of~~ (i) a water-immiscible phase comprising a water-immiscible material (e.g., pesticide) to be encapsulated and an organic polyisocyanate in (ii) an aqueous phase comprising a solution of water, a surfactant and a protective colloid; and (b) heating and maintaining said dispersion in a temperature range from about 40°C to about 90°C; where part of the water-immiscible material is encapsulated within discrete polyurea capsular enclosures.

U.S. Patent 4,285,720 deals with the encapsulation of water-immiscible substances in general and contains examples showing encapsulation of water-immiscible organophosphorus insecticides, thiocarbamate herbicides, an insect hormone mimic, and an organophosphorus flame retardant. Another example shows the encapsulation of two water-immiscible substances by this process. Various products which can

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be encapsulated are discussed generally and specifically in columns 13 and 14. This patent does not, however, mention haloacetanilide herbicides as one type of substance which may be encapsulated by the process described.

Two other patents which describe modifications or improvements to the process described in U.S. Patent 4,285,720 do include mention of haloacetanilide herbicides. U.S. Patent 4,140,516 describes the use of a phase transfer catalyst in a process such as that described in U.S. Patent 4,285,720, and mentions several haloacetanilide herbicides in column 12 to which the process may be applied. U.S. Patent 4,448,929 describes an improved protective colloid for use in the process of U.S. Patent 4,285,720 (among others) and mentions metolachlor and butachlor as two materials to which that modification may be applied.

Summary of the Invention

It has now been found that use of the process as described in U.S. Patent 4,285,720 can produce microencapsulated compositions of haloacetanilide herbicides which have the dual benefits of providing comparable herbicidal activity to nonencapsulated formulations of the same herbicide, even in the early stages of application and/or at lower application rates, while maintaining substantially lower mammalian toxicity compared with the nonencapsulated formulations.

Detailed Description of the Invention

In accordance with the invention, a microencapsulated formulation of a haloacetanilide herbicide is produced in accordance with the process described and disclosed in U.S. Patent 4,285,720. The contents of said U.S. patent are hereby incorporated by reference herein.

In brief, the process involves the encapsulation of a water-immiscible material, in this case a water-immiscible α -haloacetanilide (preferably α -chloroacetanilide) herbicide within discrete capsules of polyurea without addition of a

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second reactant. Most preferably, the herbicide is 2-chloro-N-(ethoxymethyl)-6'-ethyl-o-acetotoluidide (acetochlor). In the process, hydrolysis of an isocyanate monomer to form an amine takes place, and that in turn reacts with another isocyanate monomer to form polyurea. In general, two steps comprise the process.

In the first step, a physical dispersion of a water-immiscible phase in an aqueous phase is prepared. The water-immiscible phase comprises the haloacetanilide herbicide to be encapsulated together with other material as described below. As opposed to the process described in U.S. Patent 4,150,516, a phase transfer catalyst is not utilized (as a component of the water-immiscible or organic phase). The aqueous phase is comprised of water, a suitable surfactant, and a material termed a "protective colloid".

In the second step, the dispersion is maintained in a temperature range of from about 20°C to about 90°C during which the condensation reaction takes place to form the polyurea, at the interfaces between the droplets of the organic phase and the aqueous phase. Adjustment of the pH of the resulting mixture and the temperature within the desired temperature range during the second step advances the condensation reaction.

The aqueous phase is prepared from water, a surfactant, and a protective colloid. In general, the surfactant or surfactants in this phase may be anionic, cationic or non-ionic surfactants with an HLB range of from about 12 to about 16. Suitable surfactants include polyethylene glycol ethers of linear alcohols, ethoxylated nonylphenols, naphthalene sulfonates, and the like. Particularly preferred surfactants include block copolymers of propylene oxide and ethylene oxide and anionic/nonionic blends.

The protective colloid present in the aqueous (or continuous) phase can be selected from a wide range of such

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materials including polyalkylates, methyl cellulose, polyvinyl alcohol, polyacrylamide, poly(methylvinyl ether/maleic anhydride), graft copolymers of polyvinyl alcohol and methylvinyl ether/maleic acid (hydrolyzed methylvinyl ether/maleic anhydride; see U.S. Patent 4,448,929, which is hereby incorporated by reference herein), and alkali metal or alkaline earth metal lignosulfonates. Preferably, however, the protective colloid is selected from alkali metal and alkaline earth metal lignosulfonates, most preferably sodium lignosulfonates.

In general, the range of surfactant concentration in the process is from about 0.01 to about 3.0 percent by weight, based on the aqueous phase, but higher concentrations of surfactant may also be used. The protective colloid is generally present in the aqueous phase in an amount of from about 0.1 to about 5.0 percent by weight. The amount of protective colloid employed will depend on various factors, such as molecular weight, compatibility, etc. The protective colloid can be added to the aqueous phase prior to the addition of the organic phase, or can be added to the overall system after the addition of the organic phase or the dispersion of it.

The organic phase comprises the haloacetanilide herbicide to be encapsulated and one or more polyisocyanates. A water-immiscible organic solvent may also be used to dissolve both the haloacetanilide herbicide and the polyisocyanate. Preferably the organic phase, and at least the haloacetanilide and polyisocyanate are premixed to obtain a homogeneous phase before addition to the aqueous phase.

Depending on the nature of the haloacetanilide herbicide and the intended application or use of this microencapsulated product, the compositions of this invention may also include a herbicide safener or antidote. Many such safeners or antidotes are well known in the art. Preferred types for use with haloacetanilide herbicides include dichloroacetamides such as dichlormid (N,N-diallyl dichloroacetamide);

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2,2,5-trimethyl-3-dichloroacetyl oxazolidine (R-29148), N-dichloroacetyl-1-oxa-4-azaspiro[4,5]decane (AD-67); 4-dichloroacetyl-2,3-dihydro-3-methyl-1,4-benzoxa-zine (CGA-154281); 1-(dichloroacetyl)hexahydro-3,3,8a-trimethylpyrrolo-[1,2-a]-pyrimidin-6(2H)-one and N-(1,3-dioxolan-2-yl-methyl)-N-(2-propenyl)-2,2-dichloroacetamide (PPG-1292).

These and other dichloroacetamides are described, for instance, in U.S. Patents 4,124,372; 4,256,481; 4,294,764; 4,448,960; 4,601,745; 4,618,361; 4,708,735 and 4,900,350. Additional known types of safeners or antidotes include certain oxime derivatives (U.S. Patents 4,070,389 and 4,269,775, for instance), thiazole carboxylic acids and derivatives (U.S. Patent 4,199,506 for instance), haloacyltetrahydroisoquinolines (U.S. Patent 4,755,218, for example), aryl cyclopropane carbonitriles (U.S. Patent 4,859,232, for example) and 1,8-naphthalic acid, its anhydride and derivatives.

Safeners or antidotes, when included, will usually be contained in the organic or water-immiscible phase.

The polyisocyanates which may be used in this invention are those described in U.S. Patent 4,285,720. A single compound or a mixture of two or more polyisocyanates may be used. Mixtures are preferred. Of the polyisocyanates, polymethylene polyphenylisocyanate (PAPI), and isomeric mixtures of tolylene diisocyanate (TDI) are preferred. Particularly preferred are mixtures of polymethylene polyphenylisocyanate with isomeric mixtures of tolylene diisocyanate, in a weight ratio of PAPI:TDI of from about 1:4 to about 4:1.

The amount of the organic polyisocyanate used in the process will determine the wall content of the microcapsules formed. In general, the polyisocyanate (or microcapsule wall formed from it) will comprise from about 2.0 to about 75.0 percent by weight of the microcapsule. Most preferably the wall will comprise from about 4 to about 15% by weight, of the microcapsule.

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The haloacetanilide herbicide itself may be used as a solvent for the polyisocyanates. Alternatively, additional solvents such as xylene may be used (see Canadian Patent 1,094,402).

To obtain the appropriate dispersion, the organic phase, preferably in a premixed homogeneous state, is added to the aqueous phase, with stirring. A suitable dispersing means is employed to disperse the organic phase in the liquid phase. The means may be any high shear device, so as to obtain a desired droplet (and corresponding microcapsule particle) size within the range of from about 0.5 to about 4,000 microns. Preferably the droplet size is from about 1 to about 100 microns, most preferably from about 5 to about 20 microns, average. Once the proper droplet size is obtained, the dispersion means is discontinued. Only mild agitation is required for the remainder of the process.

To form the microcapsules, the temperature of the two-phase mixture is raised to a value of from about 20°C to about 90°C, preferably from about 40°C to about 90°C, most preferably from about 40°C to about 60°C. Depending on the system, as described in U.S. Patent 4,285,720, the pH value may be adjusted to an appropriate level.

The following are examples of preparations of compositions of this invention.

General Procedure

In the examples which follow, the compositions were prepared by the following general procedure:

The organic phase was added to the aqueous phase, and an oil-in-water emulsion was formed by means of a high shear stirrer. The average particle size was in the range of 11.0 ± 2 microns. While mild agitation was maintained, the temperature of the batch was raised to 50°C over a period of 30 minutes, and held at 50°C for 3 hours. The resulting

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microcapsule suspension was then allowed to cool to room temperature. The additional ingredients were then added and the pH was then adjusted to 11.0 with 50% caustic.

EXAMPLE I [10911-43; RF-17431]

A composition was prepared using the general procedure described above with the following ingredients.

<u>Component</u>	<u>Weight, g.</u>	<u>Weight %</u>
AQUEOUS PHASE		
protective colloid: Daxad 23 (sodium lignosulfonate)	11.6	1.43
surfactant: Pluronic L-64 (20% solution in water)	9.6	1.18
water	365.0	44.83
ORGANIC PHASE		
acetochlor (technical grade - 97.4% purity)	326.3	40.09
N,N-diallyldichloroacetamide (technical grade - 96.0% purity)	55.2	6.78
polymethylene polyphenylisocyanate	20.6	2.53
tolylene diisocyanate (mixture of 80% 2,4- and 20% 2,6- isomers)	10.5	1.29
ADDITIONAL INGREDIENTS		
suspending agents:		
attapulgate (Attagel 40)	8.0	0.98
xanthan gum (Kelzan)	0.56	0.07
buffering agent (sodium carbonate)	5.7	0.70
biocide (Proxel GXL)	0.8	0.10
flocculant (27.5% aluminum silicate)	0.2	0.02
TOTAL	814.06	100.00

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The resulting microencapsulated product had an average particle diameter (after final treatment) of 11.2 microns.

EXAMPLE II [11666-14]

Following the procedures and using the ingredients of Example 1, in similar proportions, a five-fold larger batch of product was prepared. The resulting microencapsulated product had an average particle diameter (after final treatment) of 10.2 microns.

EXAMPLE III [11666-40]

Using the general procedures described above, a composition was prepared from the following ingredients.

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<u>Component</u>	<u>Weight, g.</u>	<u>Weight %</u>
AQUEOUS PHASE		
protective colloid: Daxad 23	5.4	1.33
surfactants (anionic/nonionic blends):		
Atlox 3409F	1.1	0.27
Atlox 3404F	0.2	0.05
water	173.5	42.64
ORGANIC PHASE		
acetochlor (technical grade - 95% purity)	98.6	24.24
acetochlor (technical grade, 91.3% purity)	76.0	18.68
N,N-diallyldichloroacetamide (technical grade, 95% purity)	27.6	6.78
polymethylene polyphenylisocyanate (PAPI 135)	10.9	2.68
tolylene diisocyanate (mixture of 80% 2,4- and 20% 2,6- isomers)	5.5	1.35
ADDITIONAL INGREDIENTS		
thickener - attapulgate (Attagel 40)	4.0	0.98
thickener - xanthan gum (Kelzan)	0.28	0.07
buffer (sodium carbonate)	2.9	0.71
biocide (Proxel GXL)	0.4	0.10
flocculant (aluminum silicate)	0.5	0.12
TOTAL	<u>406.78</u>	<u>100.00</u>

The resulting encapsulated product had an average particle size (after final treatment) of 11.5 microns.

HERBICIDAL EVALUATION

The compositions prepared in the above examples were submitted for herbicidal evaluation in comparison with an emulsifiable concentrate containing the same herbicide and antidote. The emulsifiable concentrate contained 77.94 weight percent acetochlor herbicide (expressed as active ingredient), 12.97% N,N-diallyldichloroacetamide antidote, an emulsifier and Aromatic 100 xylene range solvent (Exxon Chemical Co., Houston, Texas).

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A test procedure was as follows.

Pre-emergence Surface Treatment

Seeds of the indicated plant varieties were planted in flats and watered. Sprayable solutions were prepared by diluting the microencapsulated formulations and the emulsifiable concentrate with water. About one week after planting, the flats were sprayed with the solutions at application rates ranging from 0.06 lbs./acre (0.07 kg/ha) to 2.0 lbs./acre (2.24 kg/ha). Subsequent to the spraying, the plants were evaluated for injury at the times indicated below. Injury was visually evaluated using a scale ranging from 0 to 100, with 0 representing no injury as compared to an untreated controlled flat, and 100 representing complete kill.

The results of these tests are given below in Tables I and II with the injury ratings representing an average of three replications for each test. Plants utilized in the tests are represented by the following abbreviations in these tables.

CN - corn variety T-11
SOY - soybeans, Corsoy variety
ML - milo variety R10
ROM - milo, rox orange
SV - green foxtail, *Setaria viridis*
SF - giant foxtail, *Setaria faberi*
WPM - white proso millet, *Panicum miliaceum*
SH - shattercane, *Sorghum bicolor*

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TABLE 1

rated: 19 days after treatment

<u>Test Composition</u>	<u>rate, lb./acre</u>	<u>% Injury</u>						
		<u>CN</u>	<u>SOY</u>	<u>ML</u>	<u>SH</u>	<u>SV</u>	<u>WPM</u>	<u>AVG*</u>
emulsifiable concentrate	0.06	0	18	40	77	98	63	79
	0.125	0	23	83	95	100	87	94
	0.25	15	38	95	98	100	95	98
	1.0	15	60	100	100	100	98	99
	2.0	17	78	100	100	100	100	100
microencapsulated (Ex.I)	0.06	0	25	47	70	100	85	85
	0.125	0	25	93	97	100	87	95
	0.25	0	30	95	98	100	95	98
	1.0	0	62	100	100	100	98	99
	2.0	7	70	100	100	100	100	100

* average injury to three weed species: SH, SV, WPM

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TABLE 2

rated: 32 days after treatment

<u>Test Composition</u>	<u>rate, lb./acre</u>	<u>% Injury</u>						
		<u>CN</u>	<u>SOY</u>	<u>ML</u>	<u>ROM</u>	<u>SF</u>	<u>WPM</u>	<u>AVG*</u>
emulsifiable concentrate	0.06	0	0	5	37	100	98	78
	0.125	0	12	75	91	100	95	95
	0.25	0	27	96	93	100	100	98
	0.5	0	43	98	100	100	100	100
	1.0	0	70	100	100	100	100	100
	2.0	0	72	100	100	100	100	100
microencapsulated (Ex.II)	0.06	0	0	15	37	100	98	78
	0.125	0	8	85	93	100	99	95
	0.25	0	23	88	93	100	100	98
	0.5	0	45	100	100	100	98	99
	1.0	0	63	100	100	100	100	100
	2.0	0	53	100	100	100	100	100
microencapsulated (Ex.III)	0.06	0	0	18	53	100	93	82
	0.125	0	7	93	93	100	98	97
	0.25	0	22	99	100	100	100	100
	0.5	0	45	98	100	100	100	100
	1.0	0	57	100	100	100	100	100
	2.0	0	70	100	100	100	100	100

* average injury to three weed species: ROM, SF, WPM

As can be seen from the above tables, the microencapsulated compositions prepared according to this invention performed comparably in all respects to the emulsifiable concentrate, at the same application rates.

Toxicological evaluation of a composition of this invention showed that it exhibited substantially lower mammalian toxicity as compared to emulsifiable concentrates containing acetochlor, particularly in oral toxicity tests. This combination of comparable herbicidal activity (even at low rates or early applications) and lower toxicity, compared with

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nonencapsulated compositions, is unexpected. It would normally have been expected that a substantial decrease in toxicity would be accompanied by a decrease in herbicidal effectiveness.

WHAT IS CLAIMED IS:

1. Capsules capable of controlled release of encapsulated organic material comprising 2-chloro-N-(ethoxymethyl)-6'-ethyl-o-acetotoluidide herbicide enclosed in a polyurea capsule produced by the process comprising encapsulating waterimmiscible material within discrete capsules of polyurea without addition of a second reactant, whereby hydrolysis of an isocyanate monomer to form an amine takes place which in turn reacts with another isocyanate monomer to form polyurea, which comprises the steps of: a) providing, at room temperature, a dispersion of (i) a water-immiscible phase comprising the herbicide and an organic polyisocyanate in (ii) an aqueous phase comprising a solution of water, a surfactant and a protective colloid; and b) heating and maintaining said dispersion in a temperature range from about 40°C to about 90°C, whereupon said herbicide is encapsulated within discrete polyurea capsular enclosures.
2. Capsules according to Claim 1 in which the water-immiscible phase further comprises an herbicide safener or antidote suitable for use with the herbicide.
3. Capsules according to Claims 1 or 2 in which the safener or antidote is a dichloroacetamide.
4. Capsules according to any of Claims 1 to 3 in which the protective colloid is an alkali metal or alkaline earth metal lignosulfonate.
5. Capsules according to any of Claims 1 to 4 in which the organic polyisocyanate is polymethylene polyphenylisocyanate.
6. Capsules according to any of Claims 1 to 4 wherein the polyisocyanate is an isomeric mixture of tolylene diisocyanate.

7. Capsules according to any of Claims 1 to 4 in which the polyisocyanate is a mixture of polymethylene polyphenylisocyanate and an isomeric mixture of tolylene diisocyanate.

8. Capsules according to any of Claims 1 to 4 or 7 in which the weight ratio of polymethylene polyphenylisocyanate to tolylene diisocyanate is from about 1:4 to about 4:1.

9. Capsules according to any of Claims 1 to 8 in which the dispersed water-immiscible phase comprises droplets having an average particle size of from about 5 to about 20 microns.

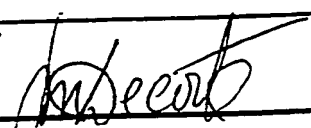
10. Capsules according to any of Claims 1 to 9 in which the organic polyisocyanate comprises from about 4 to about 15% by weight of the capsule.

11. Capsules according to any of Claims 1 to 10 containing from about 25 to about 40 weight percent herbicide, and from about 0 to about 10 weight percent of a haloacetanilide herbicide safener or antidote, and prepared using from about 0.1 to about 1.0 weight percent surfactant and about 0.5 to about 3.0 weight percent protective colloid.

INTERNATIONAL SEARCH REPORT

PCT/US 91/09284

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 A01N37/26; A01N25/28		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A01N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US,A,4 285 720 (H.B.SCHER) 25 August 1981 cited in the application see claim 1 see column 5, line 22 - column 5, line 27 see column 14, line 37 - column 14, line 39 ---	1-11
Y	EP,A,0 017 409 (MONSANTO) 15 October 1980 see claims see page 30, line 1 - page 30, line 7 see page 5, line 15 - page 5, line 18 & US,A,4 417 916 29 November 1983 cited in the application & US,A,4 280\833 28 July 1981 cited in the application ---	1-11
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
13 APRIL 1992	20. 05. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	DECORTE D.M. 	

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